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Review of mathematical investigation on the closed adsorption heat pump and cooling systems

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Abstract

A mathematical model of the closed adsorption heat pump and cooling systems is particularly used to assist in interpreting the observed phenomena, to design the system, to predict the trends, and to assist in optimization. In this paper, various mathematical models mainly analyzing the heat and mass transfer process of an adsorption bed in closed adsorption heat pump and cooling systems are reviewed and classified based on complexity, into three main groups: i.e. thermodynamic model; lumped parameters model; heat and mass transfer model. The major characteristics of different models and assumptions used are presented and discussed. Also, the numerical methods and validation of the models are summarized and significant results obtained through mathematical model are detailed. Although the models have evolved to a point where several features of the process can be predicted, more effort is required before the models can be applied to define actual operating conditions as well as to further investigate new closed adsorption cycles. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the last 20 years, interest in the closed adsorption heat pump and cooling system has been steadily increasing. One of the indications is that there are about ten review papers in this area published in recent years. Meunier [1] has summarized various solid sorption systems based on closed cycles, and has concluded that if

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Nomenclature

a	thermal diffusivity (m^2/s)
A	adsorption potential (J/mol)
c_p	specific heat at a constant pressure (kJ/ kgK)
COP	coefficient of performance
C	vapor-phase concentration (mol/m^3), Eq. (21)
C_a	adsorbate concentration (mol/kg), Eq. (20)
d_p	diameter of adsorbent particles (m)
D	effective diffusivity (m^2/s), Eq. (21)
D_{ae}	effective diffusivity (m^2/s), Eq. (20)
D_s	surface diffusion coefficient (m^2/s)
D_{s0}	pre-exponential constant in equation (m^2/s), Eq. (6)
E_0	characteristic energy used in Dubinin equation (J/mol)
E_a	activation energy of surface diffusion (J/mol)
F	criterion of error used in identification method
h	heat transfer coefficient (W/m^2K); enthalpy (kJ/m^3)
H	height of the cylindrical adsorbent bed (m)
ΔH	heat of adsorption (J/kg)
i	internal energy (kJ/m^3)
i_s	internal energy of adsorbent including adsorbate (kJ/m^3), Eq. (23)
J_b	heat flux from the heat transfer fluid into the bed, Eq. (23)
k	thermal conductivity (W/mK)
k_D	permeability of porous media (m^2)
k_E	parameter describing the inertial effect in Ergun's equation (m)
k_m	mass transfer coefficient within the pallets (s^{-1}), Eq. (4)
L	latent heat of vaporization (J/mol)
m	mass (kg)
n	specific number of moles adsorbed (mol/kg), Eq. (22); parameter of adsorption equilibrium equation
NTU	Number of Transfer Units
p	pressure (Pa)
q	mass adsorption capacity (kg/kg adsorbent)
q_0	maximum mass adsorption capacity (kg/kg adsorbent)
r	radial coordinate in the adsorbent bed
r_p	particle radial coordinate (m), Eq. (17)
R	gas constant, (J/molK); radius of the cylindrical adsorbent bed (m)
R_p	average radius of adsorbent particle
SCP	Specific Cooling Production (W/kg)
SHP	Specific Heating Production (W/kg)
t	time (s)
T	temperature (K)

u	velocity components in x directions (m/s)
V	volume
w	volume adsorption capacity, (l/kg adsorbent)
w_0	maximum volume adsorption capacity, (l/kg adsorbent)
x, y, z	axial coordinate
ε	porosity of adsorbent bed
ε_p	porosity of adsorbent particles
ε_t	total porosity
μ	viscosity (Ns/m)
ρ	density (kg/m)
τ	dimensionless time
a	adsorbate
b	bed
$cond$	condenser
e	evaporator
f	heat transfer fluid
h	high temperature heat source
mt	metal
p	particle, constant pressure
r	refrigerant
sat	saturation
t	total
V	vapor
X	axial coordinate
Z	adsorbent, axial coordinate

cooling COPs of approximately 1, with cooling rates between 300 and 1000 W/kg of sorbent can be obtained, such systems will most probably be an alternative to CFCs for refrigeration. In order to enhance the efficiencies and reduce cost on closed adsorption system, efforts made by several researchers have been summarized in yet another review paper [2]. Srivastava et al. [3] have reviewed papers on different adsorbents and absorbates used in various investigations on solid-vapor adsorption heat pumps, with the aim of initiating a novel concept experimental investigation. They have also published [4] the recent developments in adsorption refrigeration and heat pump technologies, featuring solid adsorbents as well as desiccants, emphasizing the experimental achievements.

Several research departments such as JPL/NASA, SJTU, LIMSI-CNRS etc, have been focusing on an adsorption system for several years and have achieved a lot in their specific research area. Jones [5] has described a long-life, reliable heat-powered sorption refrigeration system which had been developed for spacecraft use at the

Jet Propulsion Laboratory (JPL). Also, the design of high efficiency, ground-based adsorption heat pumps, with the addition of novel regenerative heating techniques, have been described. In China, Wang [6] has summarized research work on various adsorption refrigeration cycles being carried out in Shanghai Jiao Tong University (SJTU), which includes adsorption mechanism, thermodynamic analyses of various adsorption refrigeration cycles, high performance prototypes of an adsorption refrigerator and its application.

A recent review paper by Dieng and Wang [7], provides fundamental understanding of the solar adsorption systems and gives useful guidelines regarding design parameters of an adsorbent bed, and the applicability of solar adsorption, for air-conditioning as well as refrigeration, with an improvement in the coefficient of performance.

Although there are several review papers on adsorption heat pump and cooling systems, detailing the experimental investigations, mathematical models used in predicting the performance of adsorption refrigeration have not been summarized and listed. As such, with the development of computer hardware and numerical methodology, advanced mathematical models are being used to carry out critical investigations on an adsorption refrigeration system. The advantages of this method are that it can produce extremely large volumes of results at virtually no added expense and it is very cheap to perform parametric studies, for instance, to optimize equipment performance. The second reason for such work on numerical simulation is that the adsorption refrigeration system involves complex physical phenomena. Also, some parameters are difficult to test, and the experimental study is expensive as well as time consuming. The third reason is that, with the limitation in present technologies, some cycles, such as rotary adsorption, which still can not be presently realized but might be achieved in future with the development in related technologies, can be studied by using a numerical investigation.

In this work, a review of the present state of mathematical modeling of the adsorber or the adsorption system is given. The models are classified under three main categories: thermodynamic model, lumped parameters model, heat and mass transfer models. In general, heat and mass transfer processes are not considered in thermodynamic models. Although heat transfer is considered in the lumped parameters model, the temperature variation with space is not considered in it, which is taken care in the heat and mass transfer model. Because of similar characteristics of many of the different models, a general presentation of the group is given in the introduction of each section before discussing each particular model.

The validation is an important step in mathematical modeling development, and therefore comparisons with actual experimental values or theoretical results have been included where possible. Since most of the models have to be solved numerically, the numerical techniques employed in the solution of the different models are presented. The physical properties of adsorbent/adsorbate pairs are also summarized and the major results obtained through the mathematical model are described.

2. Thermodynamic model

2.1. Introduction

Among the different models, the model based on thermodynamic analysis is the simplest, in which details of heat transfer are not considered. In this model, only first- and second-law analysis are performed, and this kind of model can be used to reveal the upper performance limits. The first-law analysis gives a good solution to the expected performance of a cycle, and it is essential to carry out the second law analysis to study the quality of the process which, in turn, gives the reason for the performance degradation [8].

All the models are based on adsorption phenomena, no matter if the model is simple or complex. One of the major equations describing adsorption phenomena is the adsorption equilibrium equation. Hence, the adsorption equilibrium equations and the equations on adsorption heat used in thermodynamic models, lumped parameters models as well as heat and mass transfer models are summarized in Table 1.

2.2. Review of thermodynamic models

A thermodynamic model on simple and regenerative cycles based on experimental data was proposed by Cacciola and Restuccia [9]. The specific heat of refrigerant in the adsorbate phase was considered to be constant and equal to the specific heat of the gas at a given temperature and pressure. The specific heat of the dry adsorbent was also considered to be a constant. The model had been used to calculate the performances of the adsorption systems either in the heat pump or cooling operation and the useful heat/cold produced during a complete cycle per kilogram of adsorbent. The performances obtainable by three adsorbent/adsorbate pairs with regenerative cycles such as 4A zeolite-water, 13X zeolite-water, AC35 activated carbon–methanol, have been compared. The results show that zeolite/water is the most suitable pair to realize machines to be used in domestic applications in southern European countries.

Critoph [10] studied the performance limitations of adsorption cycles for solar cooling, and established a simple model based on a general study of the cycle thermodynamics. The following assumptions were made in his analysis:

- The isosteres on the ln p vs 1/T diagram were indeed linear.
- The temperature at the end of adsorption was equal to the condensing temperature.
- Constant heat source and sink temperature.
- The specific heat of the adsorbed phase was first considered to be of liquid phase, and then the sensible heat to the adsorbed phase in desorption was assumed to be equal to that needed to raise the mean mass of adsorbent during desorption to the final temperature at the end of generation.
- The liquid specific heat was assumed to be numerically equal to about 0.2% of that of the latent heat.

Table 1
A review of adsorption equilibrium equation used in different models

References	Equilibrium equation	Adsorbent–adsorbate pair	Adsorption heat
Cacciola, 1995-[9], 1999-[26] Hajji, 1995-[46], 1996-[47] Zhang, 1999a-[54] 1999b-[55], 2000-[56]	$\ln(p) = a(w) + b(w)/T$ $a(w) = a_0 + a_1 w + a_2 w^2 + a_3 w^3$ $b(w) = b_0 + b_1 w + b_2 w^2 + b_3 w^3 = \Delta H(w)/R$	4A Zeolite—Water, 13X Zeolite—Water, AC35 activated carbon—Methanol	Enthalpy of adsorption: $b(w) = b_0 + b_1 w + b_2 w^2 + b_3 w^3 = \Delta H(w)/R$
Cho, 1992-[19]	Simplified Freundlich's equation: $q = q_{sat}(P/P_{sat})^{1/n}$; q_{sat}=0.522 kg/kg, n=1.6	Fuji RD—type Silica gel–Water	
Critoph, 1988-[10]	Dubinin-Astakhov (D-A) equation: $q = W_0\rho(T)\exp[-(A/\beta E_0)^n]$	Adsorbent(Charcoal): AC35, DEG, LH, BPL, NORIT RB, PKST, 207E & C Adsorbate: NO_2,methanol, SO_2, amine, methyl, ammonia, acetonitrleand, Formaldehyde.	Clausius–Clapeyron equation: $\Delta H = \frac{R\ln(p_2/p_1)}{\frac{1}{T_1}-\frac{1}{T_2}}$
Critoph, 1998-[20,21]	Modified Dubinin -Radushkevich equation	Carbon—Ammonia	Constant
Gui, 2001-[17], 2002-[18] Wu, 2000-[28] Critoph, 2001-[35] Chahbani, 2002-[48]	Modified Dubinin-Astakhov (D-A) equation: $q = q_0\exp[-k(T/T_{sat}-1)^n]$	Active carbon—Methanol [17,18,28] Monolithic carbon—Ammonia [35]	Constant
Guilleminot, 1987-[36] Boubakri, 2000-[37] Passos, 1989-[49], Amar, 1996-[52] Mhimid, 1998-[53]	$q = W_0\rho\exp\left[-D\left(T\ln\frac{P_{sat}(T)}{P_{sat}(T_{cond})}\right)^n\right]$	Activated carbon AC-35—Methanol Activated carbon AS—Methanol Carbon AX21—Ammonia Zeolite—Water	Clapeyron equation for ideal gas: $\Delta H = RT^2(\partial\ln p/\partial T)$
Llobet, 2000-[16]	Dubinin-Astakhov (D-A) equation.	Adsorbent (activated carbon): PX21, KL93, KF1500, TA90, TA60, BPL Adsorbate: ammonia	$Q_{st}(T,P_{evap}) = RT^2[\partial\ln(p)/\partial T] = \Delta H_{NH_3} + A + 2.510^{-3}T\beta^n E_0^n A^{1-n}/n$

(continued on next page)

Table 1 (*continued*)

References	Equilibrium equation	Adsorbent–adsorbate pair	Adsorption heat
Luo, 2000-[59]	Modified Dubinin–Radushkevich Equation.: $q = q_0\exp[-k(T/T_{sat}-1)^n]$	Activated carbon AC-35—Methanol Activated carbon AC-35—Ethanol	$\Delta H = RT + L + (2303\beta/\sqrt{k}) \times [\ln^{1/2}(1/\theta) + (\alpha T/2)\ln^{-1/2}(1/\theta)]$ k,β are coefficients, α is the thermal expan-sion coefficient of liquid, and $\theta=q/q_0$
Saha, 1995-[33] Chua, 1999-[34]	$q = A(T_{ad})[P_{sat}(T_r)/P_{sat}(T_{ad})]^{B(Tad)}$ $A(T_{ad}) = A_0 + A_1T_{ad} + A_2T_{ad}^2 + A_3T_{ad}^3$ A: -6.5314, $B(T_{ad}) = B_0 + B_1T_{ad} + B_2T_{ad}^2 + B_3T_{ad}^3$ 0.72452E-1, -0.23951E-3, 0.25493E-6 B: -15.587, 0.15915, -0.50612E-3, 0.53290E-6	Silica gel—Water	Constant
Sakoda, 1984-[29],1986-[30] Saha, 1995-[31] Alam, 2000-[50]	Simplified Freundlich's equation: $q=q_{sat}(P/P_{sat})^{1/n}$ q_{sat}=0.346 kg/kg, n=1.6	Fuji-gel A type silica gel—Water	Constant
Sami, 1996-[27]	$\ln(p/p_{sat}) = \sum_i A_ic_i + (1/T_a)\sum_i B_ic_i$	Carbon–Methanol, AC–HCFC123/ HCFC124	Clapeyron equation for ideal gas
Shelton, 1990-[12] Fuller, 1994-[38]	$q = a_1 + a_2(T_z/T_{sat}) + a_3(T_z/T_{sat})^2 + a_3(T_z/T_{sat})^3$	Zeolite—Ammonia Activated carbon–Ammonia	Constant
Sun, 1995-[51] Amar, 1996-[52] Sward, 2000-[60]	$q_v = \frac{q_{s1}b_1p}{1+b_1p} + \frac{q_{s2}b_2p}{1+b_2p} + \frac{q_{s3}b_3p}{1+b_3p}q_{s,k}$ and b_k(k=1,2,3) are function of temperature	Zeolite 13X-water Zeolite 13X-ammonia	Constant
Sun, 1997-[41]	$q = 221.2\exp[-1.916\times10^{-7}(T\ln(P_s(T)/P))^n]$	Zeolite NaX- Ammonia	Constant
Zheng, 1995-[39,40]	$q=f(T_{ad},p)$	Activated carbon—Ammonia	Constant

The model was used to predict cycle COPs based on limited data available for chosen refrigerants and carbons. With activated charcoal as adsorbent, especially, it was found that, methanol, acetonitrle, methyl amine, and NO_2 are suitable among different refrigerants that are sub-atmospheric at −10 °C, but methanol gave the best COP. A similar study of refrigerants that will always be above atmospheric pressure suggests, ammonia, formaldehyde, and SO_2 are in order of merit.

Shelton et al. [11] developed a thermodynamic model for the thermal wave adsorption cycle, with certain assumptions: The temperature and adsorption profiles in the bed behave as square waves, and these waves stop short of the bed ends to account for realistic and finite wavelengths. This model is found to give good first-order results.

The authors later extended the model by assuming a more realistic ramp wave profile in the adsorbent bed [12]. Other assumptions include:

- The ramp wave had a steady-state wavy length which was related to the adsorption bed thermal design;
- The temperature was linear and the adsorption profile was obtained as a segmented ramp based on the temperature at the midpoint of the ramp.

The ramp wave model provides a simple but realistic accounting of the adsorption behavior at the bed ends, and thus a superior estimate of system behavior is possible rather than the simpler square wave model. The results had shown that heating COP on a thermal basis was of 1.6, and this efficiency was rather insensitive to the cycle's heat input and output temperatures.

A similar work was carried out by Douss and Meunier [13] and they have proposed an equilibrium model which was based on heat and mass balances for a cascading adsorption cycle in which an active carbon/methanol cycle was topped by a zeolite-water cycle. Neither kinetics effects nor temperature drops were taken into account. This model requires thermodynamic data for the adsorbent/adsorbate pair and heat capacities of all components involved in the system which are listed in the references [14,15]. The cooling COP as well as heating COP were predicted to be 0.95 and 1.54, respectively, which agreed to the experimental results within 10%.

The agreement was found to be good for condensation and evaporation when the model results were compared with the experiment, but was not so good on output heat from the zeolite adsorber and the input heat on active carbon adsorber which did not agree well with each other. It was due to the fact that: (i) contribution of heat losses in the heat balance was all the more important as driving heat supplied by boiler decreases, which was the case with cascading cycles; (ii) Dubinin's law used to represent active carbon methanol underestimate methanol cycling which was probably due to the fact that evaporating and adsorbing temperatures are close to each other.

Recently, Llobet and Goetz [16] have modeled a rotary system for the continuous operation using the concept of heat regeneration in a steady state. The system was controlled by adjusting the air flow rates and the wheel speed of rotation. The absence of valves makes the installation extremely reliable. Moreover, the system increases

the thermal potential of the air by recovering the heat of adsorption in the adsorption zone and the sensible heat of the adsorbent. The model is in the form of counter-flow heat exchanger in series.

Several assumptions were made in developing the model:

- During the pressure increase and decrease phases of the elementary modules, the pressure was considered to be imposed by the adsorbent. Conversely, during the adsorption and desorption phases, the operating pressures correspond to those of the evaporators and condensers.
- The heat transferred by contact between the adsorbent and the adsorbers-desorbers, were assumed to be negligible compared with the transfer of heat by convection between the air and the adsorbers-desorbers.
- All the elementary adsorbers-desorbers were treated as a continuous adsorbent ring rotating about the central axis of the frame and characterized by an equivalent flow rate.

The main feature of this model is the equivalent heat capacity of the elementary adsorber. In the isosteric cooling zone, the equivalent capacity of the adsorbent block consists of activated carbon, expanded graphite, composition of refrigerant and the metallic mass of the adsorber. In the adsorption zone, the equivalent heat capacity of the adsorbent additionally takes into account the change in composition of the refrigerant, the production of heat due to adsorption.

Using the above model, the COP and cold production capacity was calculated as a function of NTU and other parameters. It has been reported that the COP usually increases with an increase in NTU. The results also showed that there exists an optimal regeneration temperature which is about 170 °C for NH_3/PX21 (active carbon) pair. Several different activated carbons (PX21, KL93, KF1500, TA90, TA60, BPL) were tested, and it was found that PX21 gives the highest COP due to its greater micropore volume.

A practical model was established by Gui and Wang [17] for an endoreversible three-heat-reservoir cycle for a heat regererantion adsorption air-conditioning system. Three-heat-reservoir cycle refers to the following (Fig. 1):

1. High temperature reservoir (represented by heater temperature, T_h) supplies drive power (Q_h) for generator;
2. Low temperature reservoir (represented by temperature of supply-air from fan coil, T_f) obtains latent heat cooling power (Q_f) from evaporator;
3. Heat sink (represented by ambient temperature, T_0) at takes away the heat (Q_{01} and Q_{02}) produced in condenser and adsorber respectively.

The major governing equations in the above model are based on the first and second laws of thermodynamics, and it was assumed that the heat leak and internal irreversibility in the cycle was neglected and the adsorption process was at equilibrium. A real system prototype was constructed and a series of experiments were conducted. It was found the real thermodynamic cycle were almost the same as the

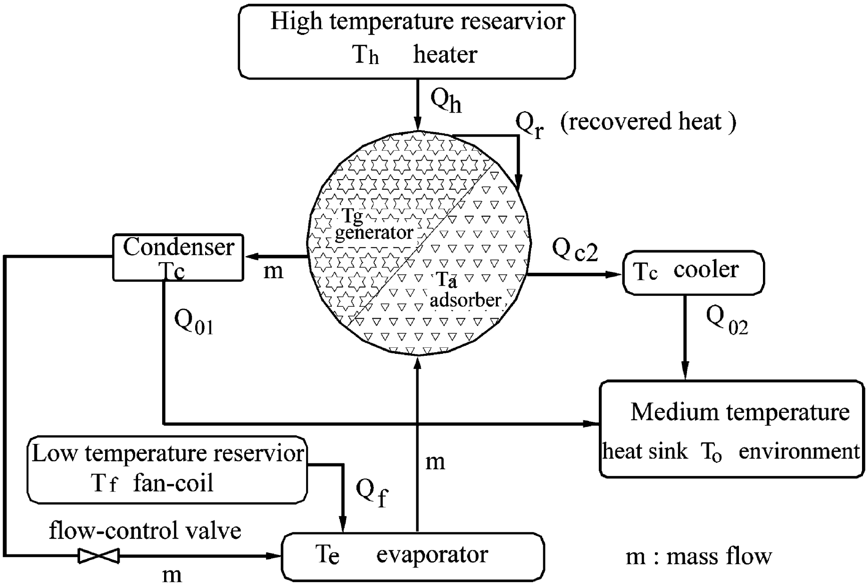


Fig. 1. Schematic diagram of heat-regenerative adsorption air-conditioning system expressed by the practical three-heat-reservoir model.

ideal cycle on the PTX chart. The effects of T_f and T_h on SCP and COP between the experiment and the practical thermodynamic model results were also compared, and it was found that the agreement was satisfactory.

Based on the above mentioned three-heat-reservoir-model, Gui et al. [18] studied the influence of various parameters on the performance of a heat-regenerative adsorptive reversible heat pump, such as temperature of the heat source, supply outlet air temperature, ambient temperature, heat capacity ratio of adsorber metal and working fluid to adsorbent etc. Four main performance indices of a heat-regenerative adsorptive reversible heat pump were studied: Coefficient of amplification (COA), Specific heating power (SHP), Heat-recovery ratio and Second law efficiency. Their results indicated that the prototype performance was satisfactory and the experimental result was close to simulation, the agreement of COA was within 8% and the agreement of SHP was within 4%.

3. Lumped parameters model

3.1. Introduction

In order to simplify the analysis based on lumped parameters, the following assumptions are generally made: (i) the temperature is uniform in the adsorbent layer; (ii) the refrigerant is adsorbed uniformly in the adsorber; and, (iii) both solid and gas phases exist at a thermodynamic equilibrium. In such models, the resistance

towards heat and mass transfer in the adsorbent are neglected. Another feature of these kinds of models is that it is usually considered as a dynamic model, i.e. temperature or mass content of the adsorbed phase changes with time.

The lumped model usually comprises three basic equations such as energy balance, mass balance and adsorption equilibrium equation. The general statement of an energy balance equation of the adsorbent bed during the desorption process is given as [19]:

$$(m_{\mathrm{mt}}c_{\mathrm{pm}} + m_{\mathrm{z}}c_{\mathrm{pz}} + m_{\mathrm{z}}qc_{\mathrm{pa}})\frac{dT_{\mathrm{z}}}{dt} = m_{\mathrm{z}}\Delta H\frac{dq}{dt} + \Phi_{\mathrm{w}\to\mathrm{z}} \tag{1}$$

Similarly, the energy equation during adsorption process is given by:

$$(m_{\mathrm{mt}}c_{\mathrm{pmt}} + m_{\mathrm{z}}c_{\mathrm{pz}} + m_{\mathrm{z}}qc_{\mathrm{pa}})\frac{dT_{\mathrm{z}}}{dt} = -m_{\mathrm{z}}\Delta H\frac{dq}{dt} + \Phi_{\mathrm{w}\to\mathrm{z}} + m_{z}c_{pa}(T_{e} - T_{z})\frac{dq}{dt} \tag{2}$$

The term in the bracket of LHS of the equations (1) and (2) includes the sensible heat of the metallic parts in the adsorber, the fully regenerated adsorbent bed, and the adsorbed phase. The first term on the RHS of equations (1) and (2) represents the heat due to adsorption and desorption process, respectively. The symbol $\Phi_{\mathrm{w}\to\mathrm{z}}$ refers to the heat transferred from the heating or cooling medium. The third term on the RHS of the equation (2) represents the sensible heat, due to the flow of refrigerant vapor from the evaporator to the adsorber.

In the model suggested by Sakoda [28], the mass balance of adsorbate was given as:

$$m_{\mathrm{z}}\frac{dq}{dt} + \frac{dm_{\mathrm{ae}}}{dt} = 0, \tag{3}$$

where 'm_{ae}' is the adsorbate in the evaporator.

3.2. Review of lumped parameters models

Douss and Meunier [14] have presented a predictive dynamic model for two adsorbers. The model is a simple lumped parameter model, and assumes that each component of the system, such as adsorber, evaporator and condenser, was homogeneous. This model is limited duly to water falling film evaporators and water condenser heat exchangers. Also, some numerical instabilities were realized, particularly at small time steps.

A dynamic model similar to the one proposed by Douss and Meunier [14] has been reported by Cho et al. [19]. In their work, in addition to the heat transported during adsorption and desorption process, the sensible heat in the continuous recirculating refrigerant was also included in this homogeneous model. Furthermore, this model analyzed the performance of a water evaporator and condenser heat

exchangers, along with that of the adsorbent bed. The overall heat-transfer coefficient for the three components (adsorber, condenser, and evaporator), estimated from the measured flow rate and temperature, have been used in the simulation. In general, the D–A equation is used to obtain the mass adsorption capacity of the adsorbate of the adsorption equilibrium. In this model, for a given range of relative pressure, the adsorption equation of the Fuji A-type silica-gel and water vapor was represented by a relation which takes into account temperature and pressure variations (listed in Table 1).

The thermal performance of the system predicted by this numerical model has shown good agreement with experimental data. Also parametric studies were performed using the model to determine the effect of the heat-transfer rate of individual components on the cold generation capacity; the heat-transfer rate of the condenser was found to be the most sensitive variable. By modifying the heat-transfer rates of the condenser and adsorber, the thermal performance could be improved by about three times. As such, this model can be utilized to investigate and optimize the adsorption-cooling system.

Critoph [20,21] proposed a lumped model to analyze the convective thermal wave which is part of a patented cycle, using heat transfer intensification to achieve both high efficiency and small size from a solid adsorption cycle. Such cycles normally suffer from low power density because of poor heat transfer through the adsorbent bed. Rather than attempting to heat the bed directly, it is possible to heat the refrigerant gas outside the bed and to circulate it through the bed in order to heat the adsorbent. The high surface area of the grains leads to very effective heat transfer with only low levels of parasitic power needed for pumping.

The cycle presented by Critoph [20,21] also utilized a packed bed of inert material to store heat between the adsorption and desorption phases of the cycle. The highest degree of regeneration possible leads to good COP. Thermodynamic modelling, based on measured heat transfer and porosity data [22], predicted a cycle COP (for a specific carbon) of 0.95 when evaporating at 0 °C and condensing at 42 °C. These temperatures are compatible with ARI conditions. But, validation of the model was not carried out. However, it was reported that a demonstration system containing a ‘one active and one inert bed’ combination is being commissioned at Warwick, UK.

Cacciola et al. [23] have presented a numerical simulation of a two-reactor adsorption heat pump, taking into account heat recovery. To simplify the analysis, two main assumptions were made: (a) uniform temperature prevailed in each reactor; (b) the adsorption process was at equilibrium. The governing energy balance equations of the adsorber, condenser and evaporator were derived, taking into account the efficiencies of various components. The equations were transformed to a non-dimensional form and solved numerically. Convergence of the numerical method was verified by varying the time step. The model was tested using the zeolite–water adsorption pair and available design data [15]. The predicted temperature variations in the adsorbent bed, condenser and evaporator were seen to be in agreement with Douss’s data [15]. This model has also been validated experimentally [24], and the program represented an efficient tool for designing a two-reactor adsorption heat pump, and

for optimizing the component sizes in order to obtain the best system performance [24,25].

Based on the above work Cacciola et al. [26] presented a simplified dynamic model in integral form, to evaluate the performance of an adsorption heat pump when heat transfer in the adsorbent reactors is the only cycle-time limiting factor. This generalized approach excludes the influence of the mass transfer and of other heat pump components, such as the evaporator and condenser. The two main equations used in this model were the time equation and energy equation, derived from energy balance. The time equation was used to calculate the time period of different phases. To study the influence of this adsorber heat exchanger design, two different cases had been considered in the model as a function of the relation between the final temperature of the reactor at the end of the heat recovery step and the initial adsorption temperature.

The simulation aimed to study the effect of an increased amount of metal in the adsorbent of metal in the adsorbent bed on the COP and on the specific power. This correspondingly affects the energy delivered to the user and the investment cost of the system.

It was shown that an increase in the heat capacity ratio of the metal and the dry zeolite, increases the heat transfer inside the reactor beds, and results in a minimum value of heat transfer characteristic (ratio of overall heat transfer to the mass of adsorbent), in order to have at least the same cost per unit power. It has been reported that an improvement in heat transfer can be achieved by increasing the metal content of the adsorber bed, but may result in a reduction in COP and can eventually increase the investment cost per watt obtained. Hence, it is an important factor to be considered when the effort is being made to increase the heat transfer in the reactor beds. As the proposed method is independent of the reactor size and type, and excludes other components in the heat pump system, it is a useful method for comparison of different solutions, for improvement of the performance and economics of heat pump systems.

Sami and Tribes [27] presented an improved lumped parameter model for single and/or double adsorber with heat recovery. The mathematics for simulation of this model was based on conservation equations and the isosteric equation of state. Several constitutive relationships had been integrated into the model to enhance its capability to predict the thermal phenomena that takes place inside the adsorber and the heat exchangers. The heating phase equation is similar to the equations used by Douss and Meunier [15]; however, the cooling phase equation contains an additional term to account for the thermal effects due to the flow of refrigerant vapor from the evaporator to the adsorber (the third term on the RHS of equation (2)). New submodels were added to predict the performance of an air-cooled evaporator and condenser-type heat exchangers. The heat transfer coefficient was calculated using related heat transfer correlation with respect to the variation of the temperature along the adsorber, which has shown to represent a significant improvement in the prediction of the adsorber thermal behavior, compared to the model presented in Ref. [15]. The discretized governing differential equations were solved for each control volume,

and the updated values of the system's variables were obtained by numerical integration in time.

Experimental data of a double adsorber cycle with heat recovery presented by Refs. [1,15], had been simulated to assess the validity of their proposed model in predicting the adsorption cascading cycle. The authors have demonstrated that this model predicted the temperature of the adsorber well, as well as the other parameters of the adsorption system and compares well with the experimental data. Based on the reliability of their model, they also carried out simulations using the pair active carbon and HCFC-123/HCFC-124 mixture. This particular mixture was selected since it has a high boiling temperature. The simulation results indicated that lower heat capacities were obtained with the use of the HCFCs mixture which was mainly due to low latent heat of evaporation and condensation, at the simulated conditions, compared to methanol.

The model developed by Wu et al. [28] is similar to the one proposed by Sami et al. [27]. In their study, a novel shell and tube type heat exchanger was adopted as the adsorber, however, the effects of the heat exchanger were not analyzed. Based on the experimental conditions simulated by using the proposed model, experimental work was carried out. In the simulation certain operational parameters, such as the cycle time, temperature of the heat source, cooling water and the overall heat transfer coefficient of the adsorber, were determined in accordance with the experimental data. In contrast, the heat transfer coefficients in Sami's model [27] were determined using Dittus–Boelter correlation for smooth tubes. Hence, in Wu et al's work [28], the experimental results were in close agreement with the calculated data of the dynamic simulation.

Sakoda et al. [29] proposed a model which takes into account both adsorption properties and apparatus characteristics on the solar powered adsorption cooling system using silica-gel and water pair. One of the important features of this model is that, it includes a mass balance equation of adsorbate in the lumped model. The model includes three main equations such as mass balance equation of adsorbate, heat balance equation of the packed beds of adsorbents and a separate heat balance equation for the evaporator. In the model, the adsorption uptake was approximately given by the linear driving force (LDF) expressed by the difference of the amount adsorbed (q), and the maximum amount adsorbed (q_0) in equilibrium at certain pressure conditions.

$$\frac{dq}{dt} = k_m(q_0 - q) \tag{4}$$

$$k_m = 15D_s/R_p^2 \tag{5}$$

$$D_s = D_{so}\left(-\frac{E_a}{RT}\right). \tag{6}$$

The theory proposed was not a complete one and was considered as a first-step model for estimating operation with any practical equipment. To improve on the results, the work was further extended [30] by considering different temperatures

between the container of adsorbents and the adsorbent particles. Heat balance of the container of adsorbents and that of adsorbent particles are expressed respectively. Parameters used in the model were classified into four main categories:

- adsorption properties, obtained from fundamental experiments;
- parameters determined based on design conditions of the container of adsorbents and the evaporator;
- parameters given by environmental or operating conditions;
- heat transfer coefficients, estimated using empirical correlation.

This quantitative analysis for the simultaneous transport of heat and adsorbate in the operation of a closed-type solar-powered adsorption cooling system had shown that, it can successfully interpret the experimental results. Further, the results have clearly shown that the solar COP of a system is controlled by the efficiency given as the ratio of the heat used for regeneration of adsorbents to the total solar heat input, and also that the efficiency is governed by the heat transfer area between the container of adsorbents and the inner adsorbent particles.

Saha et al. [31] proposed a simulation program similar to Sakoda [29] for a two bed silica gel-water adsorption chiller. The adsorption equilibrium equation was obtained by adopting the Freundlich equation [31] using the manufacturer's experimental data. The simulation was carried out to verify the influence of operating temperatures (hot and cooling water), water flow rates, and adsorption–desorption cycle times. It was found that the operating temperature, followed by water flow rates were the most influential parameters on COP of the system. Also, it has been reported that cycle time was less influential in quantitative terms, but still qualitatively it was very important.

As the second part of their study on the use of adsorption refrigeration cycles driven by waste heat of near-ambient temperature [32], experiments were conducted with several heat transfer fluid operating temperatures. Also, the effect of different flow rates, adsorption–desorption cycle times were also studied. Both experiments and simulation showed that the silica gel-water adsorption cycle is well suited to near-enviromental-temperature heat sources and small regenerating temperature lifts, which help reduce the heat losses intrinsic to batched cycle operation. The chiller was operational with a hot water-inlet temperature of 50 °C, and the highest experimental values of the COP (more than 0.4) were obtained with this water-inlet temperature in combination with cooling water at 20 °C.

However, further work is required in the development of advanced cycles for operation with even smaller regenerating temperature lifts (e.g. 50 °C driving heat source and 30 °C cooling source) as well as improved heat exchangers to enhance heat transfer and reduce heat losses. Using the above model, Saha et al. [33] investigated analytically the performance of the thermally driven, advanced three-stage adsorption chiller utilizing low-grade waste heat of 50 °C and lower temperatures as the driving heat source, in combination with a heat sink (cooling water) of 30 °C. The main advantage of this chiller is that it is operational with smaller regenerating temperature lifts (heat source—heat sink temperature) than other heat-driven chillers.

By cycle simulation, it was shown that the three-stage chiller can be operated with heat sources of 50 and 40 °C in combination with cooling source of 39 and 30 °C, respectively.

Chua et al. [34] have also worked on the model proposed by Saha et al. [31] to gain a deeper understanding of the two bed, silica gel-water adsorption chiller but without heat recovery. This type of chiller has already been commercialized in Japan and its schematic is given in Fig. 2. Chua et al. [34] improved the simulation program by reconstructing the governing equation using the number of discrete elements in the heat exchanging tubes of the beds, evaporator and condenser in order to account for the accurate temperature variation at different sections of the tubes. The effects of different initial refrigerant mass distribution in various components on the transient performance of the chiller were presented, and the results showed the chiller was able to achieve a unique cyclic-steady-state condition within four cycles or 1800s.

The entire chiller operation, consisted of one cooling phase and one switching phase. During the cooling phase, one adsorber was cooled by a coolant so as to maintain the adsorption process and another adsorber was heated by the heat source to maintain the desorption process. The role reversal was achieved by switching the flow of heat source and coolant in the beds. During the switching period, the valves connecting the beds to the condenser and evaporator were shut, while the hot bed was cooled by the coolant and the cold bed heated by the heat source.

They also demonstrated that the manufacturer-prescribed switching and cycle time tended to give rise to close to maximum cooling capacity operation. Further, under standard rated conditions, the recommended fixed switching time strategy had comparable effects on suppressing the peak evaporator temperature to that of the more

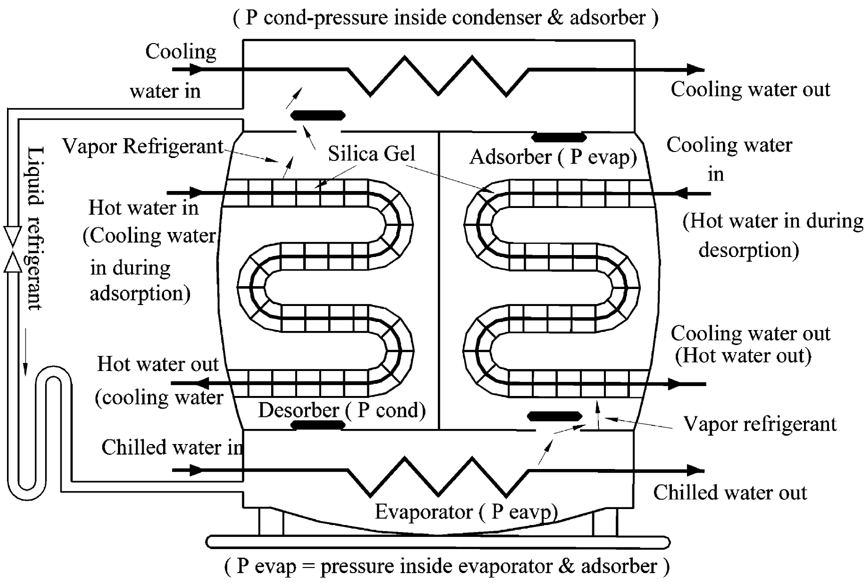


Fig. 2. Schematic of a two-bed adsorption chiller commercialized in Japan.

sophisticated chamber pressure equalization strategy. This shows that, simply by judiciously selecting the switching time, the same favorable conditions can equally be achieved, albeit under more restricted operating conditions, by a more cost effective option. All these confirm the view that the manufacturer had empirically evolved to achieve maximum cooling capacity from a compact chiller.

Critoph [35] had described a new, continuous rotary adsorption refrigeration system and had patented it. This system is similar to the rotary system introduced by Llobet and Goetz [16], in which the module is provided with an adsorbent bed along the outer circumference of the tube. In the rotary system proposed by Critoph [35], the module was provided with an adsorbent bed inside the tube, as a closed section. The schematic of a section of the rotary system showing the details of a single module is given in Fig. 3, which comprises a generator and a receiver/condenser/evaporator. The refrigerant flowing in the module is similar to that of the working media in a heat pipe. A prototype unit was fabricated and tested at laboratory scale. Using simple governing equations, the performance of the above system, consisting of 32 modules, was predicted. The effect of key parameters such as thermal capacity ratio, number of modules, generator heat transfer coefficient and evaporator air inlet temperature on the system performance was also studied. It has been reported that future work will be carried out in optimizing the above system, and also an attempt would be made to discover the ideal limitations of the concept by using second law analysis.

4. Heat and mass transfer model

4.1. Introduction

As said earlier, among the different models available in the literature, the simulation based on heat and mass transfer are very significant, since they give insight into the dynamics of the adsorber in a adsorbent cooling system. A heat and mass transfer model is featured in which temperature or mass content of adsorbate varies not only with time but also with space and the governing equations are always partial differential equations. As such it is important for proper/optimum design of adsorption machines. Based on the geometry of the adsorber, the models can be grouped under one-dimensional, two-dimensional and three-dimensional models. The differ-

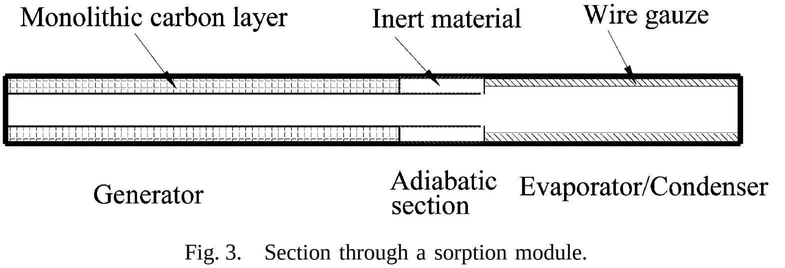


Fig. 3. Section through a sorption module.

ence among various models used to simulate adsorptive cooling units, generally lies on the differences in the simplifying assumptions, numerical resolution method, design and use of the modeled system.

In general, heat and mass transfer on adsorbent bed solid adsorbents involves four main governing equations such as: energy balance equation, mass conservation equation, momentum equation and state equation of the adsorbent-adsorbate system. These equations are usually nonlinear, due to the adsorption isotherms and physical properties, and become even more complex to solve if the adsorption process is considered as a cyclic process with varying boundary and initial conditions.

If the system is considered to be one-dimensional, the mathematical model will be based on the following equations:

The overall refrigerant mass conservation is described as:

$$\varepsilon\frac{\partial(\rho_{\mathrm{v}})}{\partial t}+\frac{\partial(\rho_{\mathrm{v}}u)}{\partial x}+\rho_{\mathrm{z}}\frac{\partial q}{\partial t}=0. \tag{7}$$

For the diffusion within a particle in the adsorbate, a mass balance over the particle can be written as follows:

$$\frac{\partial(q)}{\partial t}=\frac{\partial}{\partial x}\left(\rho D_{\mathrm{s}}\frac{\partial q}{\partial x}\right). \tag{8}$$

Conservation of momentum is given by:

$$\frac{\partial(\rho u_{\mathrm{v}})}{\partial t}+\frac{\partial(\rho u_{\mathrm{v}}u_{\mathrm{v}})}{\partial x}=-\frac{\partial p}{\partial x}-\frac{\partial}{\partial x}\left(\mu\frac{\partial u_{\mathrm{v}}}{\partial x}\right). \tag{9}$$

The Energy balance equations for vapor and solid adsorbent can be given as:

$$\varepsilon\frac{\partial(\rho_{\mathrm{v}}c_{\mathrm{pv}}T_{\mathrm{v}})}{\partial t}+\frac{\partial(\rho_{\mathrm{v}}c_{\mathrm{pv}}u_{\mathrm{v}}T_{\mathrm{v}})}{\partial x}=\frac{\partial}{\partial x}\left(\varepsilon k_{\mathrm{v}}\frac{\partial T_{\mathrm{v}}}{\partial x}\right)+\frac{\partial(c_{\mathrm{pv}}\rho_{\mathrm{z}}q)}{\partial t}(T_{\mathrm{v}}-T_{\mathrm{z}})-h_{\mathrm{vz}}(T_{\mathrm{v}}-T_{\mathrm{z}}) \tag{10}$$

and

$$\rho_{\mathrm{z}}(c_{\mathrm{pz}}+c_{\mathrm{pa}}q)\frac{\partial T_{\mathrm{z}}}{\partial t}=\frac{\partial}{\partial x}\left[k_{\mathrm{z}}(1-\varepsilon)\frac{\partial T_{\mathrm{z}}}{\partial x}\right]+\rho_{\mathrm{z}}\Delta H\frac{\partial q}{\partial t}+h_{\mathrm{vz}}(T_{\mathrm{v}}-T_{\mathrm{z}}). \tag{11}$$

The complexity and nonlinearity of such coupled heat and mass transfer models in general exclude the possibility of having an analytical solution. Therefore, numerical methods are the only feasible alternative to meet the requirements for simulation of adsorbent bed dynamics. Numerical methods used include the finite difference method [36,46,52,54], the finite volume method [53] and the finite element method [49]. The finite difference method is frequently utilized due to its simplicity, efficiency in solving parabolic equations and ease of varying initial and boundary conditions. In order to simplify the numerical analysis, involving heat and mass transfer, certain assumptions are made which can be grouped under four categories: (i) thermodynamic state; (ii) thermophysical properties and material properties; (iii) heat source, condenser and evaporator; (iv) heat and mass transfer.

Of the various models reported on this topic there are two main approaches. The first deals with heat transfer but does not take into account mass transfer, while the second solves the energy equation and the equation of motion simultaneously. The present review first discusses the 'non-rigorous' and later the 'rigorous' models. A summary of the main features of each model is given in Table 2.

4.2. Review of models on heat transfer phenomena

A uniform pressure model has been presented by Guilleminot et al. [36] to describe the heat transfer in a fixed bed of solid adsorbent in a finned reactor of rectangular cross-section (shown in Fig. 4). This model neglects the resistances to mass diffusion but takes into account the resistances to heat diffusion through two coefficients: the heat conductivity of the adsorbent bed and the heat transfer coefficient between the adsorbent bed and the fins.

The mathematical formulation of the system was based on two energy conservation equations written for copper (Eq. (12)) and the adsorbent layer (Eq. (13)), with an assumption that the heat source was at constant temperature.

$$\rho_{\mathrm{mt}} c_{\mathrm{mt}} \frac{\partial T_{\mathrm{mt}}}{\partial t} = k_{\mathrm{mt}} \left(\frac{\partial^2 T_{\mathrm{mt}}}{\partial x^2} + \frac{\partial^2 T_{\mathrm{mt}}}{\partial y^2} \right), \tag{12}$$

$$\rho_{\mathrm{z}} (c_{\mathrm{pz}} + q c_{\mathrm{pa}}) \frac{\partial T_{\mathrm{z}}}{\partial t} = \rho_{\mathrm{z}} \Delta H \frac{\partial q}{\partial t} + k_{\mathrm{z}} \left(\frac{\partial^2 T_{\mathrm{z}}}{\partial x^2} + \frac{\partial^2 T_{\mathrm{z}}}{\partial y^2} \right). \tag{13}$$

In the above equation, the mass source term was obtained from the state equation of the bivariant solid-vapour equilibrium. The initial temperature, pressure, and mass distribution conditions were assumed to be uniform. This numerical method uses the finite-difference technique according to a Crank-Nicholson schema. For the explicit method, the very great ratio between the thermal diffusivity of the copper wall and that of the bed requires the use of a time step of the order of 1/1000 s, which, in view of the overall time of a complete cycle (of the order of a few hours) made the above numerical simulation prohibitive. An experiment was conducted to validate this model, and the two heat transfer coefficients of the adsorbent bed and that of fins, were obtained by an identification technique.

When the temperature of the closed reactor was modified on one side of the reactor, large temperature inhomogeneities inside the reactor were observed and mass transfer occurred through a heat pipe effect: the model could explain the effect that was observed experimentally. This uniform pressure model is more adapted to describe the history of solid adsorbent reactors used in thermal processes than uniform temperature models proposed by other authors.

A similar extension of Guilleminot et al.'s model [36] was carried out by Boubakri et al. [37], to simulate the operating performance of an adsorptive solar-powered ice-maker, and was validated experimentally. Three unknown heat transfer coefficients relating the condenser, evaporator and ice-making tank were obtained by using the same identification method used by Guilleminot et al.[36]. This global model could also estimate the limits of ice production by means of adsorptive collec-

Table 2
Features of heat and mass transfer models reviewed in present work[a]

References	Governing equations	Dimension of governing equations for adsorbent bed	Cycle	Adsorber characteristic
Guilleminot, 1987–[36]	2EB: reactor wall, bed	Two-dimensional	Not specificed	Rectangular elementary cell
Boubakri, 2000–[37]	2EB: reactor wall, bed	Two-dimensional	Solar powered intermittent cooling system	Rectangular, packaged component (collector-condenser)
Fuller, 1994–[38]	2EB: heat transfer fluid, bed	One-dimensional	Heat regenerative two-beds heat pump	Spiral heat exchanger
Zheng, 1995–[39,40]	3EB: heat transfer fluid, tube wall, bed	One-dimensional	Two-beds heat pump	Not specified
Sun, 1997–[41]	3EB: heat transfer fluid, tube wall, bed	One-dimensional	Thermal wave heat regeneration heat pump	Cylindrical shape adsorber
Hajji, 1995–[46],	1EB: bed	One-dimensional	Intermittent cooling system	Rectangular cross section
Hajji ,1996–[47]	1EB: bed	Two-dimensional	Intermittent cooling system	Rectangular cross section
Chahbani, 2002–[48]	2EB: tube wall, bed 3 sub-models on mass transfer kinetics	Two-dimensional	Not specified	Cylindrical shape adsorber
Passos, 1989–[49]	1EB: bed linear driving force (LDF) equation.	Two-dimensional	Solar powered intermittent cooling system	Rectangular elementary cell
Alam, 2000–[50]	2EB: heat transfer fluid, bed (including reactor wall) linear driving force (LDF) equation.	Two-dimensional	Two-beds heat pump	Cylindrical shape adsorber
Sun, 1995–[51]	3EB: heat transfer fluid, tube wall, bedmass balance (bed), Ergun equation.	One-dimensional	Thermal wave heat regeneration heat pump	Cylindrical shape adsorber
Amar, 1996–[52]	3EB: heat transfer fluid, tube wall, bed mass balance (bed), Darcy equation.	Two-dimensional	Thermal wave heat regeneration heat pump	Cylindrical shape adsorber

(*continued on next page*)

Table 2 (*continued*)

References	Governing equations	Dimension of governing equations for adsorbent bed	Cycle	Adsorber characteristic
Mhimid, 1998–[53]	Gas energy balance, solid energy balance, mass balance (bed) linear driving force (LDF) equation. Darcy equation.	Two-dimensional	Not specified	Cylindrical shape adsorber
Zhang, 1999a-[54] 1999b-[55], 2000–[56]	4EB: heat transfer fluid, tube wall, fin, bed mass balance (bed) linear driving force equation (LDF) Darcy equation.	Three-dimensional	Intermittent cooling system	Cylindrical shape adsorber with fins
Tather, 1999–[57]	1EB: bed mass balance (bed—effective diffusity)	One-dimensional	Intermittent heat pump	Cylindrical shape adsorber (adsorbent synthesized on the tube surface)
Luo, 2000–[59]	1EB: bed mass balance (bed—effective diffusity)	One-dimensional	Solar powered intermittent cooling system	Cylindrical shape adsorber
Sward, 2000–[60]	1EB: bed mass balance (bed)	One-dimensional	Thermal wave heat regeneration heat pump	Cylindrical shape adsorber

[a] EB: Energy Balance equation

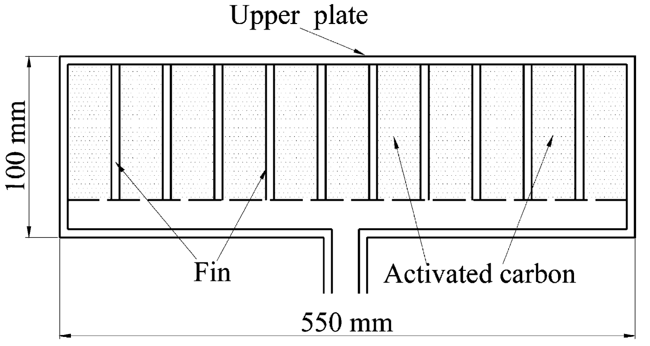


Fig. 4. Cross-section of the reactor showing the upper plate, the fins and the packing of the active carbon between the fins.

tor-condenser technology: the daily ice production (D.I.P.) could reach about 11.5 kg per m^2 of collector and the corresponding COP was about 19%. This represents the limit of collector–condenser technology with flat plate collectors.

In the above mentioned models, the heat transfer of the working fluid has not been taken into account. Fuller et al. [38] had presented a simple one-dimensional uniform pressure heat transfer model of a heat regenerative two-beds heat pump, in which the spiral type adsorbent beds are modeled using a two-temperature approach. The “two temperature” refers the assumption that the adsorption pair, heat transfer fluid tube, and outer shell (collectively known as the bed), at a given radius and time, are at the same temperature while the heat transfer fluid is at a different temperature. The governing equations include two energy balance equations, one on the fluid control volume and the other on the bed control volume. The adsorption equilibrium equation was derived from a least squares curve fit of experimental adsorption data.

Similar to Fuller’s simulation, Zheng et al. [39,40] also derived a one-dimensional uniform pressure heat transfer model of a heat regenerative two-beds heat pump. The macropore and micropore mass transfer resistance in the sorbent beds were assumed to be negligible. Their model is a “three temperature” model. Hence, the governing equations include three energy balance equations: (i) of the heat transfer fluid, (ii) the tube wall and the (iii) for the adsorbent. With the assumption of large conduction resistance in the flow direction in the heat transfer fluid and the sorbent layers, the diffusion term in the flow direction had been omitted in the energy balance equations.

The energy equations were expressed non-dimensionally and had been solved using the implicit difference method. The accuracy of their computational program had been verified in three manners: firstly, changing the step size to ensure grid-size independence; secondly, comparing their simulation results to the numerical results given by others, and finally, comparing their predictions to experimental results obtained by others.

A widely used numerical model [41,42,43,44] which might be first presented by

Sun et al. [41] can be considered as an extension of the model of Zheng et al. [39]. The diffusion term in the flow direction was included in the energy balance equation in the "three temperature" model. This model was used to investigate various aspects of the thermal wave heat-regeneration heat pump. The principle of this kind of heat pump is shown in Fig. 5. The solid curves in the adsorbers, heating system and cooling systems show the fluid temperature profiles. The temperature gradients through the adsorbers are large: the energy transmitted to the adsorber in the heating period is much larger than that supplied by the heat source. Since the adsorber is of cylindrical shape and the circulating heat transfer fluid can be located either inside or outside the adsorbent bed, the three differential equations used in the system analysis are listed below:

$$\frac{\partial T_{\mathrm{f}}}{\partial t} + v\frac{\partial T_{\mathrm{f}}}{\partial z} - D_f\frac{\partial^2 T_{\mathrm{f}}}{\partial z^2} - \frac{h_{\mathrm{f}}S_{\mathrm{f}}}{V_{\mathrm{f}}\rho_{\mathrm{f}}c_{\mathrm{f}}}(T_{\mathrm{f}} - T_{\mathrm{m}}) = 0 \tag{14}$$

$$V_{\mathrm{mt}}\rho_{\mathrm{mt}}c_{\mathrm{mt}}\frac{\partial T_{\mathrm{mt}}}{\partial t} + h_{\mathrm{f}}S_{\mathrm{f}}(T_{\mathrm{mt}} - T_{\mathrm{f}}) + h_{\mathrm{z}}S_{\mathrm{z}}(T_{\mathrm{f}} - T_{\mathrm{z}}) = 0 \tag{15}$$

$$\rho_{\mathrm{z}}V_{\mathrm{z}}(c_{\mathrm{pz}} + qc_{\mathrm{pa}})\frac{\partial T_{\mathrm{z}}}{\partial t} = \rho_{\mathrm{z}}V_{\mathrm{z}}\Delta H\frac{\partial q}{\partial t} + h_{\mathrm{z}}S_{\mathrm{z}}(T_{\mathrm{f}} - T_{\mathrm{z}}). \tag{16}$$

The above set of equations were solved numerically using an implicit finite difference method with the second order Crank–Nicolson scheme. The spatial discretization in the axial direction was done with a constant step. For the spatial discretization in the radial direction, with circulating fluid being presented in the inside adsorber, an equal spacing was used. When the heat transfer fluid (HTF) was considered to be outside the adsorber, an iso-volumetric discretization was applied. This iso-volumetric discretization has been proved to be considerably more efficient than the equal-spacing discretization by Sun et al. [45]. The time constants for heat exchange and heat conduction in the adsorbent bed were derived using the moment analysis and were used to quantify the relative importance of the two heat transfer

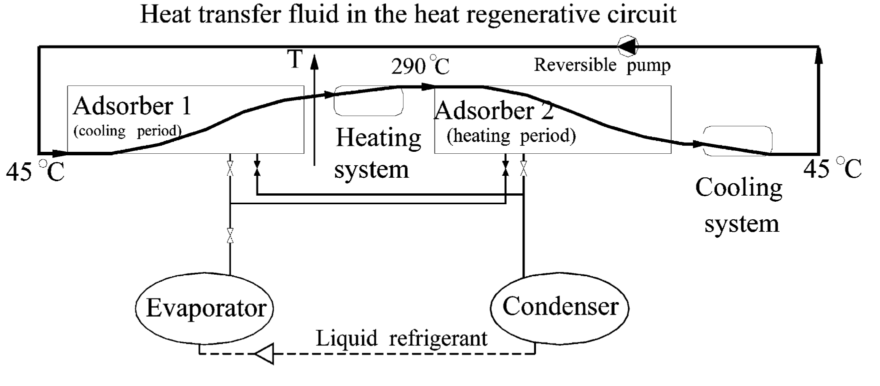


Fig. 5. Principle of thermal wave heat-regeneration heat pump.

process. The effects of the thermal conductivity and the cycle time on the process were also presented.

The above described model was also used by Pons and Feng [42] to investigate the effect of the number of transfer units (NTU) and the dimensionless outlet fluid temperature at the end of the cold front in the adsorptive refrigeration cycles using thermal regeneration. In order to reduce the internal irreversibility of the adsorption cycles with thermal wave heat regeneration, Szarzynski et al. [43] used the above model to investigate different internal vapour transports for pressurizing (depressurizing) the adsorber. First, adiabatic direct pressurization (depressurization) with the condenser (evaporator) instead of pressure changes by heat transfer; second, adiabatic internal vapour recovery between the adsorbers (partial pressurization/depressurization); third, separation of the adsorber into separate compartments to avoid a heat pipe effect [36]. It has been reported that the first process significantly reduces the COP, while the second one enhances the cooling power, and the third one does not change the performance.

In most of the above models, material thermophysical properties are often assumed to be constant. However, this assumption is valid when the material undergoes small temperature changes and in the case of large temperature changes, possible errors may be done when using this assumption. Pons and Szarzynski [44] modified the model proposed by Sun et al. [41] to analyze the role played by the changing density and specific heat of the heat transfer fluid in the heat regenerative adsorption cycles for refrigeration. Due to the changes in the fluid density, the continuity equation was added into the governing equations to account for the change of fluid velocity. Results obtained with the assumption of constant density and/or constant heat capacity were compared to those obtained with temperature dependent density and heat capacity. It was realized that the assumption on density had no influence on the COP, but, the temperature dependence of heat capacity could not be neglected. Assuming a constant heat capacity led to over-estimated performance and to optimal operating conditions that were rather different from the ones calculated with a non-constant heat capacity.

Hajji and Khalloufi [46] presented a one-dimensional model which is almost the same as that of Guilleminot et al. [36], with certain modifications. They had simplified the model by assuming the constant heating/cooling fluid temperature. The non-dimensional definite difference equations were solved using an explicit method, and the solutions were validated by comparing the predicted temperature profile with that obtained from the analytical expression using the mean values of the apparent specific heat and thermal conductivity. An experimental study was also carried out to test and validate the model. Agreement with experimental data indicated that the present one-dimensional model gave reasonably accurate results and was also confirmed by a two-dimensional model developed later in order to analyze the improvement of sorption kinetics by inserting metallic fins in the adsorbent material [47].

The parametric analysis using this two-dimensional model revealed that a significant improvement of sorption kinetics can be obtained by reducing the distance between the fins and the contact resistance at the interface metal-adsorbent. However, the thickness of the fin and the nature of the metal have a very low effect on the

improvement. It has been recommended that thin fins and cheap metals should be used to minimize the price of the cost and weight of the system.

4.3. Review of models on heat and mass transfer phenomena

Most of the above models, based on heat transfer phenomena, assume that thermodynamic equilibrium exists between the solid and liquid phases explicitly or implicitly [9,36–47]. Thermodynamic equilibrium includes two aspects in adsorption phenomena: mass equilibrium and thermal equilibrium. In mass equilibrium models, it is assumed that there exists no resistances to mass transfer between the gaseous and solid. The adsorbed amount was simply related to the gas pressure and the adsorbent temperature through the adsorption equilibrium equation.

To investigate the effect of intraparticle mass transfer limitations, Chahbani et al. [48] established a one-dimensional model in which three different sub-models were used to describe refrigerant transfer between gaseous and solid phases. The model of the adsorber consists of dynamic heat balances for the tube (similar to Eq. (15)), the adsorbent bed (similar to Eq. (16)), and the mass transfer kinetic equations.

The mass transfer kinetic equations broadly covered the following:

- The linear driving force model—in which, the parabolic concentration profile within the particle was assumed and adsorption uptake was approximated using Eqs. (4) and (5).
- The solid diffusion model—in which, the gas diffusion in a spherical particle was governed by Fick's law, and the mass balance over the particle was given as:

$$\frac{\partial q}{\partial t} = \frac{1}{r_p^2}\frac{\partial}{\partial r_p}\left(r_p D_s \frac{\partial q}{\partial r_p}\right) \tag{17}$$

- The mass equilibrium model.

The equations were first written in dimensionless form and then were discretized using the central differencing scheme. The resulting system of ordinary differential and algebraic equations were solved by the DASSL integration algorithm of Petzold [48] which is the modified version of Newton's method.

The model proposed by Passos et al. [49] was a two-dimensional uniform pressure model similar to the one proposed by Guilleminot et al. [36]. However, a linear driving force (LDF) equation (Eqs. (4) and (5)) was additionally introduced to account for the resistance to mass transfer within the pellets [29]. The finite element method was used and the numerical solution was compared to experiments performed on a solar-powered icemaker in Orsay. A good agreement was obtained on the history of the temperatures, as well as on the history of the desorbed mass of methanol.

The study also reports that for the activated carbon–methanol pair, it does not depend much on the heat transfer coefficients in the reactor; and it depends still less on the mass transfer coefficients within the reactor. Also, the overall solar COP could be improved by about 20% if one used the activated carbon AS proposed by Passos et al. [49] instead of the active carbon AC-35 used in Orsay.

In the investigation made by Alam [50], two-dimensional heat transfer equations were established for both the fluid and adsorbent sides. This study analyzed a set of non-dimensional parameters, which presented the different physical design and operating parameters of the system. A parametric study was also conducted to show the effects of different non-dimensional parameters on the system performances and their results were similar to the results obtained by Hajji et al. [46] as well as Zheng et al. [39].

In general, to analyse any adsorptive heat pump applications, a uniform pressure condition is assumed [31–35,38–44], since mass transfer resistances in the bed voids and the macropores inside the adsorbent particles are negligible. This assumption is acceptable in basic solid/vapor adsorption cycles, in which, cycle time is long and major resistances result only from heat transfer. However, with improved heat transfer properties and the use of a long adsorbent bed, mass transfer may become rate limiting.

Sun et al. [51] developed a model to study the performance of a long cylindrical adsorbent bed, with external fluid heating. Besides the heat balance equations which are similar to Eqs. (14)–(16), the mass balance of refrigerant in the adsorbent bed was also considered as one-dimensional. The superficial velocity of the gaseous phase in the bed void was determined by the Ergun equation [51]:

$$u + \frac{\rho}{\mu} k_{\mathrm{E}} u^2 = -\frac{k_{\mathrm{D}} \partial p}{\mu\, \partial x}. \tag{18}$$

The dimensionless partial differential equations were solved by a finite difference method using Crank–Nicolson scheme. For spatial derivatives, diffusion terms were replaced by the central differencing which has a third consistency. Similarly, the convection term in the fluid equation was approximated by a third order quadratic upstream differencing scheme. The numerical results were compared to the analytical solution obtained in some simplified limiting cases: plug flow with a finite rate exchange and equilibrium dispersed plug flow. The agreement seems to be good and this numerical method gives a better description of the dynamic behavior of heat transfers.

The above model was extended by Amar et al. [52] to numerically analyze an adsorptive heat pump system with the temperature wave heat regeneration. In this mathematical formulation, the heat balance equations for the thermal fluid and tube were one-dimensional, but the heat and mass balance equations in the adsorbent bed were two-dimensional. The flow velocity of the gaseous adsorbate was estimated using the Darcy’s law [52].

$$u = -\frac{k_{\mathrm{D}} \partial p}{\mu\, \partial x}. \tag{19}$$

These equations were numerically solved using the alternating direction implicit (ADI) finite difference method. The convection terms were approximated by the quadratic upstream differencing scheme and the diffusion terms were replaced by the centered difference analogs, similar to Sun et al. [51].

Simulations were performed on two adsorption systems: aeolite NaX—water and

activated carbon AX21—ammonia. The consideration of both heat and mass transfer in the model had made it possible to determine the impact of the convective transport of the gaseous adsorbate in the adsorber on the global performance, in addition to that of the heat transfer. It is reported that with a traditional packed bed, which generally has a low thermal conductivity (~0.2 W/mK), the performance of the resulting heat pump was very poor.

Mhimid [53] established two numerical models for two-dimensional transient heat and mass transfer during water desorption by zeolite bed to study the validity of a thermal equilibrium assumption [38–52]. It is possible to determine the time–space evolution of state variables such as temperature and moisture content, using the above two numerical models.

The mathematical formulations were solved using the finite volume method. The main advantage of this method is to ensure flux conservation, and thus avoid generation of parasitic sources. An implicit scheme was adopted to avoid numerical instabilities and the models were used to determine the total mass desorbed.

A more complex, three-dimensional heat and mass transfer numerical analysis was proposed by Zhang et al. [54–56]. This model included four submodels: heat transfer in heating/cooling fluids, heat transfer in the metal tube, heat transfer in the fins, and heat and mass transfer in the adsorbent. Both the internal and the external mass transfer resistance in the adsorber have been taken into account. The adsorber was a cylindrical coaxial tube (Fig. 6) with heat transfer fluid flowing through the inner tube, and an adsorbent layer in the space between the inner and outer tube. Twelve radial fins were symmetrically distributed in the adsorbent to intensify heat conduction in the bed. A linear driving force equation was introduced to account for mass transfer resistance within the pallets (internal mass transfer resistance), as proposed by Sakoda and Suzuki [29,30]. Similarly, the vapor velocity in the porous media (external mass transfer resistance) was determined by Darcy's law [52].

Numerical results showed that the proposed model predicted the dynamic response of the adsorption system well, compared with experimental data. It also gives a tool for optimization of adsorption systems driven by solar heat or other low-grade heat.

The temperature, pressure, velocity and water uptake fields of the bed and their

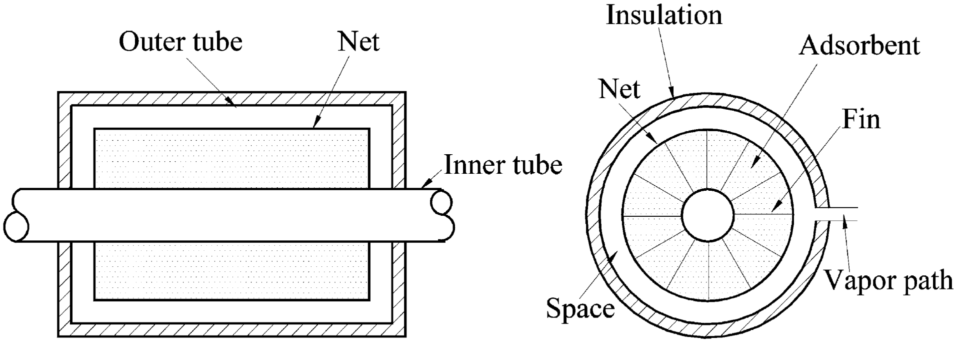


Fig. 6. Schematic of the adsorber showing two tubes, the fins, the net, the insulation and the adsorbent.

effects on system performance were also studied by Zhang and Wang [55]. It was found that for the isosteric phase, besides conduction, the heat pipe effect plays an important role in heat and mass transfer On the other hand, for the isobaric phase, there was no obvious heat pipe effect. The mass was transferred radially except at the two ends of the beds where axial mass transfer prevailed.

The above model was also used to investigate the effects of heat and mass transfer on the system performance of an automobile waste heat adsorption cooling system [56]. It was found that the system performance can be strongly influenced by the adsorber configurations such as the fin numbers, the adsorbent thickness, and the heat transfer coefficients. Furthermore, the performance of the system can seriously deteriorate through poorer mass transfers in the adsorbent, if its permeability is less than the critical value.

Tather et al. [57] developed a mathematical correlation for a novel arrangement proposed in order to cope with the drawbacks originating from the poor heat exchange at the metal-adsorbent interface. The zeolite is envisioned to be synthesized on the surfaces of heat exchanger tubes as a continuous coating, which was also achieved experimentally. The mass transfer equation in the governing equations is different from that of other models [51–56]. In Tather et al.'s model, it is assumed that the mass transfer is merely due to diffusion and that no convection occurs in the adsorbent bed:

$$(1/D_{\mathrm{ae}})\frac{\partial(C_{\mathrm{a}})}{\partial t}-(1/r)\frac{\partial(C_{\mathrm{a}})}{\partial r}-\frac{\partial^2 C_{\mathrm{a}}}{\partial r^2} = 0. \tag{20}$$

The boundary conditions were simplified using the scaling method [55] and a finite difference scheme was employed to obtain the variation of the temperature of the adsorbent, as well as the concentration of the adsorbate within the adsorber. It was observed that the typical restrictions of adsorption heat pumps were removed to a great extent, and the duration of a single cycle could be significantly shortened. The same mathematical model was used to determine the cycle duration for different thicknesses of the zeolite layer and the heat exchanger tube wall [58].

A study of an annular type adsorber, intended to account for transient temperatures observed experimentally, was carried out by Luo and Tondeur [59]. This transient model accounts for the coupling of adsorption and heat transfer, and describes mass transfer in the annular adsorbent layer as a global diffusional mechanism with temperature dependent parameters. The mass balance equation used in this analysis was simplified (using effective diffusitivity of refrigerant) and was given as:

$$\varepsilon\frac{\partial C}{\partial t} + (1-\varepsilon)\rho_{z}\frac{\partial q}{\partial t} = \frac{\varepsilon\partial C}{r\,\partial r}\left[Dr\frac{\partial C}{\partial r}\right]. \tag{21}$$

This model could correctly predict, qualitatively and semi-quantitatively, the experimentally observed trends of the temperature changes. Their study had shown that a lumped model, not accounting for the detailed profiles in the adsorbent, would not give correct predictions of the transient evolutions. On the other hand, a relatively simple model accounting for these profiles distinctly improves the predictions if one neglects the very short pressure transients.

Sward et al. [60] have proposed a model for a thermal wave adsorption heat pump cycle, in which the heat transfer fluid flows axially and is in thermal contact with the bed. Local equilibrium was assumed to provide the asymptotic best-case performance.

For each section of the bed, the material balance $f(z)$, consisted of an adsorbed-phase term, a gas-phase term, a flow term, and was given as:

$$\rho_b \frac{\partial n}{\partial t} + \frac{\partial(\varepsilon_t C)}{\partial t} + \frac{\partial(\varepsilon_b u_v C)}{\partial z} = f(z). \tag{22}$$

Similarly, the energy balance for the bed consisted of the above mentioned four terms, plus a term for heat transfer flux through the bed walls (J_b).

$$\rho_b \frac{\partial i_s}{\partial t} + \frac{\partial(\varepsilon_t i_v)}{\partial t} + \frac{\partial(\varepsilon_b u_v h_v)}{\partial z} = J_b + g(z) \tag{23}$$

where, $g(z)$, describes energy fluxes into and out of the bed through inlet and outlet valves.

The above equations were converted into dimensionless form, discretized into a number of individual cells of certain length and written into the ordinary differential equations, and the equation set was integrated numerically by Gear's method utilizing the package LSODE [60]. The model was utilized to examine the performance of adsorption refrigeration cycles powered by low temperature waste heat sources of 373–393 K. The impact of varying system temperatures, bed cycling frequency, valve positioning, and sectioning of the bed were examined.

The results showed that the location of inlet/outlet valves in the bed was found to have an impact on the shape of the temperature and loading fronts. The introduction of partitions within the bed was found to have only a small impact on the performance of the cycle for the temperatures examined, with sections of the bed undergoing pressurization in a non-sequential order.

5. Conclusion

A good many approaches or correlations have been developed for simulating the performance of an adsorption heat pump/refrigeration system. In this work, a review is given of the present state of mathematical modeling under three different categories based on thermodynamic aspects and lumped parameters as well as coupled heat and mass transfer.

Thermodynamic models are usually expressed in algebraic or relatively simple equations and are based on the steady state of the system. Certain assumptions used in the mathematical formulation appear to be too ideal. However, these models are useful in qualitative or semi-quantitative analysis of the system, and in general, they are used to study the influence of temperature and heat transfer on system COP and specific cooling power, for different adsorbent/adsorbate pairs. Unlike the thermodynamic models, lumped models are considered to be transient models and are usu-

ally expressed in ordinary differential equations. The focus is primarily on the adsorbent bed, however, geometry of the adsorbent bed is not considered in the model.

Of the three fundamental quantities considered for modeling purposes, the energy component is the one that has received most attention. Not much work has been done on the mass transfer effects, possibly because of the complex nature of the adsorption process. These models are commonly expressed in partial differential equations and can be used to find the most detail information. They serve as a design tool and are frequently used to study the effect of various geometric parameters, operating parameters on the system performance. Indeed, they are used to investigate the validity of various assumptions.

Because of the complex nature of the nonlinear ordinary and partial differential equations, it is necessary to use numerical methods to obtain the solutions. The numerical method used includes the finite difference method, the finite volume method and the finite element method. The finite difference method is the most frequently utilized and the implicit formulation is often used to minimize the instabilities which arise due to the nonlinear nature of the governing equations.

Model validation is a key step in model development since it offers the possibility of comparing computed results with actual system behavior. Experiments are mostly used to validate the mathematical model as well as in finding important parameters for modeling, such as heat transfer coefficients [43,44]. However, other methods are also used, such as comparison with known analytical solutions, or previous numerical results. Good agreement is generally observed and the computed trends are also comparable to those reported for experimental observations. However, there appears to be a lack of agreement among authors in several areas and furthermore, there are still some key deficiencies that can only be addressed through continued enhancement of the existing modeling techniques. As such, there exists a large body of work to predict several features of the process. More effort is required before the models can be applied to optimal design of the system, define actual operating conditions, as well as to investigate further new closed adsorption cycles.

Future work should be directed towards a more comprehensive description of the mass transfer phenomena, which would involve the generation of more information in the thermodynamic properties of the systems of interest, definition of reaction mechanisms, and a more fundamental approach linking the fluid flow and heat transfer results with the mass transfer events.

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